

(19)日本国特許庁 (JP)

(12) 公開特許公報 (A)

(11)特許出願公開番号

特開平6-275269

(43)公開日 平成6年(1994)9月30日

| | | | | |
|--------------------------|------|--------|-----|--------|
| (51)Int.Cl. ⁵ | 識別記号 | 庁内整理番号 | F I | 技術表示箇所 |
| H 0 1 M 4/58 | | | | |
| 4/02 | D | | | |
| 10/40 | Z | | | |

審査請求 未請求 請求項の数2 O L (全 6 頁)

(21)出願番号 特願平5-62265

(22)出願日 平成5年(1993)3月22日

(71)出願人 000002325

セイコー電子工業株式会社

東京都江東区亀戸6丁目31番1号

(71)出願人 000108007

セイコー電子部品株式会社

宮城県仙台市太白区西多賀5丁目30番1号

(72)発明者 坂田 明史

東京都江東区亀戸6丁目31番1号 セイコー電子工業株式会社内

(72)発明者 岩崎 文晴

東京都江東区亀戸6丁目31番1号 セイコー電子工業株式会社内

(74)代理人 弁理士 林 敬之助

最終頁に続く

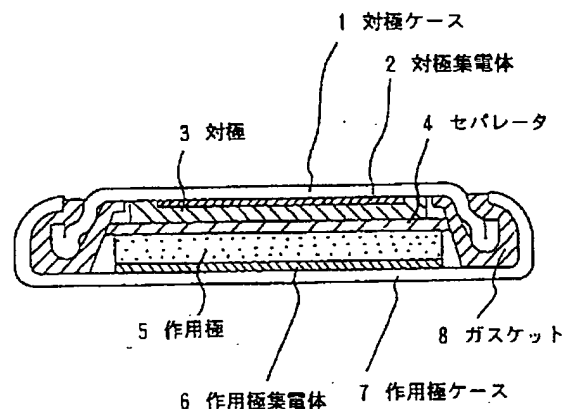
(54)【発明の名称】 非水電解質二次電池及びその製造方法

(57)【要約】

【目的】 充放電特性が優れ、且つサイクル寿命の長い新規な非水電解質二次電池及びその製造方法。

【構成】 負極と正極とリチウムイオン導電性の非水電解質とから少なくとも成る非水電解質二次電池において、負極活物質として、組成式 RMO_3 で示されるペロブスカイト型構造の酸化物又は、これにリチウムを含有させて得られる複合酸化物 Li_xRMO_3 を用いる。

【効果】 充放電容量が大きく高エネルギー密度であり、かつ充放電時の分極（内部抵抗）が小さいため大電流充放電が容易であると同時に、過充電過放電による劣化が小さく、サイクル寿命が長い。



THIS PAGE BLANK (USPTO)

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 06-275269

(43)Date of publication of application : 30.09.1994

(51)Int.Cl.

H01M 4/58

H01M 4/02

H01M 10/40

(21)Application number : 05-062265

(71)Applicant : SEIKO INSTR INC
SEIKO ELECTRONIC
COMPONENTS LTD

(22)Date of filing : 22.03.1993

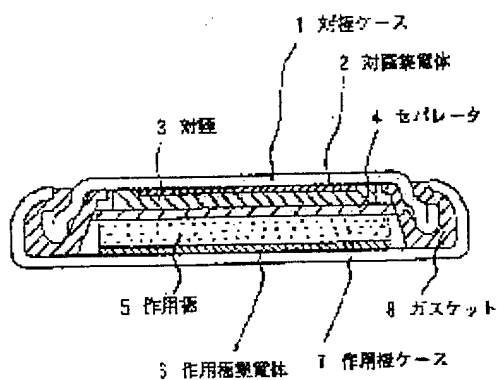
(72)Inventor : SAKATA AKIHITO
IWASAKI FUMIHARU
YAHAGI SEIJI
TAWARA KENSUKE
ISHIKAWA HIDEKI

(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY AND ITS MANUFACTURE

(57)Abstract:

PURPOSE: To provide a new nonaqueous electrolyte secondary battery excellent in charge/discharge characteristics and having a long cycle life and provide its manufacture.

CONSTITUTION: A nonaqueous electrolyte secondary battery is constituted of at least a negative electrode 3, a positive electrode 5, and a lithium ion conducting nonaqueous electrolyte. An oxide having the perovskite structure and expressed by the composition formula RMO_3 or a composite oxide Li_xRMO_3 containing lithium in RMO_3 is used for a negative electrode active material. Charge/discharge capacities are large, large-current charge/discharge can be easily made, the deterioration due to overcharge/overdischarge is small, and the cycle life is long.



CLAIMS

[Claim(s)]

[Claim 1] It sets to the nonaqueous electrolyte rechargeable battery which consists of a negative electrode, a positive electrode, and the nonaqueous electrolyte of lithium ion conductivity at least, and is an empirical formula RMO_3 as a negative-electrode active material. Nonaqueous electrolyte rechargeable battery characterized by using the oxide of the perovskite type structure shown, or the multiple oxide Li_xRMO_3 which this is made to contain a lithium and is obtained.

[Claim 2] It is in an after [cell assembly] cell, or it sets on the way of a cell production process, and is the oxide RMO_3 of perovskite type structure within a cell and out of a cell. The manufacture approach of the nonaqueous electrolyte rechargeable battery according to claim 1 characterized by depending on an electrochemical reaction with the matter containing a lithium or a lithium, making the oxide of perovskite type structure contain a lithium, and obtaining this multiple oxide (Li_xRMO_3).

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention uses as a negative-electrode active material the matter which can occlusion emit a lithium, and about the nonaqueous electrolyte rechargeable battery using the nonaqueous electrolyte of lithium ion conductivity, especially, they are a high voltage and a high energy consistency, and a charge-and-discharge property is excellent, and it relates to the new negative-electrode active material which offers the new long rechargeable battery of a cycle life.

[0002]

[Description of the Prior Art] The nonaqueous electrolyte cells using a lithium as a negative-electrode active material are a high voltage and a high energy consistency, and are already widely used as power sources the object for memory backup, for cameras, etc. as a primary cell with the advantage of ** -- self-discharge is small excellent in dependability over a long period of time. However, with remarkable development of the electronic equipment of a pocket mold, communication equipment, etc., the device which requires a high current output from the cell as a power source appears variously, from a viewpoint of the formation of small lightweight of economical efficiency and a device, re-charge and discharge are possible, and the rechargeable battery of a high energy consistency is demanded strongly in recent years. for this reason, although the researches and developments which advance rechargeable battery-ization of said nonaqueous electrolyte cell which has a high energy consistency are done actively and put in practical use in part, energy density, a charge-and-discharge cycle life, dependability, etc. are **** -- it is ** -- it is inadequate.

[0003] Conventionally, as positive active material which constitutes the positive electrode of this kind of rechargeable battery, it depends on the gestalt of a charge-and-discharge reaction, and the thing of three sorts of following types is found out. The 1st

type is types which only a lithium ion (cation) depends on an intercalation, a day intercalation reaction, etc., and go in and out between the layers of a crystal, and between a grid location or an interstice, such as a metal chalcogen compound of TiS_2 , MoS_2 , and NbSe_3 grade, and a metallic oxide of MnO_2 , MoO_3 , V_2O_5 , LiXCoO_2 and LiXNiO_2 , and $\text{Li}_x\text{Mn}_2\text{O}_4$ grade, like **. The 2nd type is a type like conductive polymers, such as the poly aniline, polypyrrole, and poly para-phenylene, with which only an anion mainly depends and frequents stability at a dope and a dedope reaction. The 3rd type is types (an intercalation, a day intercalation or a dope, dedope, etc.) with which both lithium cations and anions like **, such as conductive polymers, such as intercalated graphite and the poly acene, can go in and out.

[0004] As a negative-electrode active material which, on the other hand, constitutes the negative electrode of this seed cell, although the output voltage as a cell which the case where a metal lithium was used independently combined with the positive electrode using the above positive active material since electrode potential was ** most was the highest and the energy density was also highly desirable, in connection with charge and discharge, the dendrite and the non-**** compound generated on the negative electrode, degradation by charge and discharge was large, and there was a problem that a cycle life was short. In order to solve this problem, as a negative-electrode active material The alloy of (1) lithium and other metals, such as aluminum, Zn, Sn, Pb, Bi, and Cd, (2) -- WO_2 , MoO_2 , and Fe_2O_3 and TiS_2 etc. -- an inorganic compound and graphite -- The intercalation compound which carried out occlusion of the lithium ion into crystal structures of **, such as a carbonaceous ingredient which calcinates the organic substance and is obtained, or an insertion compound, (3) Using the matter which can occlusion emit the lithium ion of **, such as conductive polymers which doped the lithium ion, such as the poly acene and polyacethylene, is proposed.

[0005]

[Problem(s) to be Solved by the Invention] However, generally, since the electrode potential of these negative-electrode active materials is ** from the electrode potential of a metal lithium when a cell is constituted combining **, the negative electrode using the matter which can occlusion emit lithium ions other than the above metal lithiums as a negative-electrode active material, and the positive electrode using the above positive active material, there is a fault of falling considerably from the case where the operating potential of a cell uses a metal lithium independently as a negative-electrode active material. For example, in using a lithium and alloys, such as aluminum, Zn, Pb, Sn, Bi, and Cd, at 0.2-0.8V, and a carbon-lithium intercalation compound, 0.5 - 1.5V operating potential falls with the lithium ion insertion compound of 0-1V, MoO_2 , or WO_2 grade.

[0006] Moreover, since elements other than a lithium also turn into a negative-electrode component, the capacity and energy density per volume and per weight fall remarkably. furthermore, when the alloy of the above-mentioned lithium of (1) and other metals is used The use effectiveness of the lithium at the time of charge and discharge is low, and a crack occurs in an electrode by the repeat of charge and discharge, and there is a problem that a cycle life is short, for producing a crack etc. In the case of the lithium intercalation compound of (2), or an insertion compound There is degradation of collapse of the crystal structure, generation of the irreversible matter, etc. by fault charge and discharge. Moreover, since there is much what has high (it is ****) electrode potential, There is a fault that the output potential of the cell using this is low, and in being the conductive

polymer of (3), there is a problem that charge-and-discharge capacity, especially the charge-and-discharge capacity per volume are small.

[0007] For this reason, in order to be a high voltage and a high energy consistency, and for a charge-and-discharge property to be excellent and to obtain the long rechargeable battery of a cycle life, the larger negative-electrode active material of the amount, i.e., effective charge-and-discharge capacity, which can carry out occlusion emission of the lithium ion reversibly [there is no degradation of collapse of a crystal structure, generation of the irreversible matter, etc. to which the electrode potential to a lithium depends on occlusion emission of the lithium ion at the time of charge and discharge low (it is ****), and] is required.

[0008]

[Means for Solving the Problem] This invention raises using the new matter which consists of the multiple oxide which the oxide RMO_3 of the perovskite type structure shown with an empirical formula Li_xRMO_3 is made to contain a lithium as a negative-electrode active material of this kind of cell, and is obtained and which can be lithium ion occlusion emitted in order to solve the above troubles. That is, a lithium is contained in the crystal structure by using the oxide (RMO_3) of perovskite type structure as starting material, it depends on electrochemical reaction in nonaqueous electrolyte, and the multiple oxide which emits [occlusion and] a lithium ion is used. As elements R and M which constitute the oxide of perovskite type structure, one kind of the element which can generate oxides of the perovskite type structure of **, such as a metal of others, such as transition metals, such as alkali metal, such as alkaline earth metal, such as Mg, calcium, and Ba, and Li, Na, K, and Fe, Mn, Ti, V, Nb, Co, nickel, and Zn, Cd, Pb, Sn, or two kinds or more are used, respectively.

[0009] The presentation ratio of element R:M:O (oxygen) which constitutes the oxide of such perovskite type structure produces the non-stoichiometric compound which depends on the deficit of R and M which often constitute the oxide of perovskite type structure on the occasion of composition, or Oxygen O although 1:1:3 is a criterion as mentioned above, and although the range of the deficit therefore differs in the class of R and M, it reaches to **10%. The thing of such an indeterminate ratio presentation is also contained in this invention. In using transition metals as M, using alkaline earth metal, Pb, or Sn as R which constitutes the oxide of perovskite type structure especially Since it is easy to generate R and M which constitute the oxide of this perovskite type structure, or the high compound of whenever [by the deficit of Oxygen O / indeterminate ratio], There are many sites which can carry out occlusion of the lithium ion in the crystal structure of a product, and there is an advantage -- the high thing of whenever [electronic conduction] which has the high mobility of a lithium ion is obtained, and the thing with a large and charge-and-discharge capacity which has small polarization is easy to be obtained -- and it is advantageous. Especially, Pb is set to M as R, the case of PbTiO_3 using Ti is good, and the charge-and-discharge property is especially excellent. Moreover, especially the range of $0 \leq x \leq 2$ is [that what is necessary is just the range where this multiple oxide exists in stability as a content x of a lithium] desirable.

[0010] As the desirable manufacture approach of this multiple oxide of the oxide RMO_3 of perovskite type structure and the lithium which are used as a negative-electrode active material of this invention cell, although the following approach is raised, limitation is not carried out to these. That is, it is the approach of depending on an electrochemical

reaction with the matter containing the perovskite mold oxide (RMO3), the above-mentioned lithium, or above-mentioned lithium like PbTiO3, CaVO3, SrVO3, CaCrO3, SrCrO3, SrCrO3, MnTiO3, SrTiO3, BaTiO3, SrCoO3, BaPbO3 and CaTiO3, and CaFeO3 **, carrying out occlusion of the lithium ion to the oxide (RMO3) of this perovskite type structure, and obtaining the multiple oxide of the oxide of perovskite type structure, and a lithium.

[0011] As matter containing the lithium for using for this electrochemical reaction, the matter which can occlusion emit a lithium ion which is used for positive active material or a negative-electrode active material raised by the term of the above-mentioned Prior art can be used, for example. The occlusion of the lithium ion which depends on the electrochemical reaction to such oxide (RMO3) of perovskite type structure is in an after [cell assembly] cell, or can be performed within a cell and out of a cell in the way of a cell production process, and can specifically be performed as follows.

[0012] What fabricated the mixture in the predetermined configuration is used as one electrode (operation pole). namely, mixing with the oxide (RMO3) of (1) this perovskite type structure or them and an electric conduction agent, a binder, etc. -- Make two electrodes the matter containing a metal lithium or a lithium counter in contact with the nonaqueous electrolyte of lithium ion conductivity as another electrode (counter electrode), and an electrochemistry cel is constituted. How to energize or discharge with the suitable current for the direction in which an operation pole carries out a cathode reaction, and to carry out occlusion of the lithium ion to the oxide (RMO3) of this perovskite type structure electrochemically. This obtained operation pole is used as an active material which constitutes a negative electrode or a negative electrode as it is, and a nonaqueous electrolyte rechargeable battery is constituted. (2) mixing with the oxide (RMO3) of this perovskite type structure or them and an electric conduction agent, a binder, etc. -- fabricate a mixture in a predetermined configuration and include in a nonaqueous electrolyte rechargeable battery by using as a negative electrode what the alloy of a lithium or a lithium etc. was stuck by pressure or contacted to this, and used it as the laminating electrode at it. The approach by which self-discharge of a kind of local battery is formed and carried out, and occlusion of the lithium is electrochemically carried out to the oxide (RMO3) of this perovskite type structure when this laminating electrode touches an electrolyte within a cell. (3) Use the oxide (RMO3) of this perovskite type structure as a negative-electrode active material, contain a lithium in a positive electrode and constitute the nonaqueous electrolyte rechargeable battery using the matter which can occlusion emit a lithium ion as an active material. The approach by which occlusion of the lithium ion emitted from the positive electrode by charging as a cell at the time of use is carried out to the oxide (RMO3) of this perovskite type structure.

[0013] Thus, the multiple oxide Li_xRMO_3 containing the lithium obtained is used as a negative-electrode active material. Especially the negative electrode that uses as an active material the multiple oxide Li_xRMO_3 which depends on this invention Since the charge-and-discharge capacity of the **** field not more than 1V has the large electrode potential to a metal lithium and degradation to which it depends on overcharge overdischarge is small, the above-mentioned V_2O_5 , Li_xCoO_2 and Li_xNiO_2 , and $\text{Li}_x\text{Mn}_2\text{O}_4$ And it excels in a high current charge-and-discharge property. etc. -- the electrode potential to a metal lithium like a metallic oxide combines with 3V or the positive electrode using the active material of high potential beyond 4V -- a high-voltage high

energy consistency -- Since the small rechargeable battery of degradation by overcharge overdischarge is obtained, it is especially desirable.

[0014] On the other hand as an electrolyte, gamma-butyrolactone, propylene carbonate, Ethylene carbonate, butylene carbonate, dimethyl carbonate, Diethyl carbonate, methyl formate, 1, 2-dimethoxyethane, independent or the mixed solvent of organic solvents, such as a tetrahydrofuran, dioxolane, and dimethyl formamide, -- as a supporting electrolyte -- LiClO_4 , LiPF_6 , LiBF_4 , and LiCF_3SO_3 etc. -- the organic electrolytic solution which dissolved the lithium ion dissociative salt -- What is necessary is just nonaqueous electrolyte of lithium ion conductivity of **, such as inorganic solid electrolytes, such as the giant-molecule solid electrolyte or Li_3N which made said lithium salt dissolve to giant molecules, such as polyethylene oxide and the poly FOSUFAZEN bridge formation object, and LiI .

[0015]

[Function] Empirical formula RMO_3 of this invention The oxide of the perovskite type structure shown, or multiple oxide Li_xRMO_3 which this is made to contain a lithium and is obtained Occlusion emission of the lithium can be repeatedly carried out [in the inside of nonaqueous electrolyte] to stability to a metal lithium in the range of the electrode potential of 0-3V at least (an intercalation, a day intercalation or a dope, dedope, etc.), and it can be repeatedly used for the negative electrode used as an active material as a negative electrode of the rechargeable battery in which charge and discharge are possible according to such electrode reaction. It has the high capacity field which carries out occlusion emission and can carry out the repeat charge and discharge of the lithium ion to stability in the **** potential field of 0-1V especially to a lithium criteria pole.

Moreover, greatly [it is remarkable, the amount, i.e., the charge-and-discharge capacity, which can carry out occlusion emission of the lithium ion reversibly compared with carbonaceous ingredients such as graphite conventionally used as a negative electrode of this kind of cell, and], since polarization of charge and discharge is small, the charge and discharge in a high current are possible, degradation of decomposition, crystal collapse, etc. by overcharge overdischarge is hardly seen further, but it is very stable and the long cell of a cycle life can be obtained.

[0016] Thus, although the reason the outstanding charge-and-discharge property is acquired is not necessarily clear, it is presumed as follows. That is, the multiple oxide Li_xRMO_3 which the oxide (RMO_3) of the perovskite type structure which is a new active material by this invention is made to contain a lithium, and is obtained has the high mobility of the lithium ion in the inside of this structure, and since there are very many sites which can carry out occlusion of the lithium ion, it is presumed because occlusion emission of a lithium ion is easy.

[0017] Hereafter, an example explains this invention to a detail further.

[0018]

[Example]

(Example 1) Drawing 1 is the sectional view of the coin mold cell in which an example of the test cell used for the performance evaluation of the electrode active material of the nonaqueous electrolyte rechargeable battery which depends on this invention is shown. In drawing, 1 is a counter electrode case which serves as a counter electrode terminal, and carries out spinning of the plate made from stainless steel which carried out nickel plating of outside one side. 2 is a counter electrode charge collector which consists of the

network made from stainless steel, and spot welding is carried out to the counter electrode case 1. A counter electrode 3 pierces a given thickness Mino aluminum plate in diameter of 15mm, fixes to the counter electrode charge collector 2, and sticks by pressure what pierced the given thickness Mino lithium foil in diameter of 14mm on it. 7 is the operation pole case made from stainless steel which carried out nickel plating of outside one side, and serves as the operation pole terminal. 5 is the operation pole constituted using the comparison active material which depends on the active material which depends on below-mentioned this invention, or a conventional method, and is pasted up on the operation pole case with the operation pole charge collector 6 which consists of electroconductive glue which makes carbon a conductive filler. 4 is a separator which consists of a porosity film of polypropylene, and the electrolytic solution sinks in. an operation pole case opening edge bends it inside at the same time 8 is a gasket which makes polypropylene a subject, intervenes between the counter electrode case 1 and the operation pole case 7 and maintains the electric insulation between a counter electrode and an operation pole -- having -- caulking **** -- therefore, cell contents are sealed and closed to things. An electrolyte is lithium perchlorate LiClO_4 to volume ratio 1:1:2 mixed solvent of propylene carbonate, ethylene carbonate and 1, and 2-dimethoxyethane. What was dissolvedl. one mol /was used. The magnitude of a cell was 1.6mm in the outer diameter of 20mm, and thickness.

[0019] The operation pole 5 was produced as follows. Commercial lead titanate PbTiO_3 What depended on the automatic mortar and carried out the grinding particle size regulation to the particle size of 53 micrometers or less is used as the active material 1 which depends on this invention. this -- as an electric conduction agent -- graphite -- as a binder -- bridge formation mold acrylic acid resin etc. -- the weight ratio 65:20:15 -- comparatively -- coming out -- mixing -- an operation pole -- a mixture -- carrying out -- a degree -- this operation pole -- a mixture -- 2 ton/cm² Pressing was carried out to the with a diameter thickness [0.3mm thickness of 15mm] pellet, and the operation pole 5 was produced. Then, after pasting up this operation pole 5 on the operation pole case using the operation pole charge collector 6 which consists of conductive resin adhesives made into a carbon system conductivity filler and unifying, the above-mentioned coin form cell was produced using what carried out heating under reduced pressure desiccation for 10 hours at 200 degrees C.

[0020] Moreover, the same graphite was used as an active material (an active material 4 and brief sketch) with having used for the above-mentioned electric conduction agent instead of the active material 1 which depends on above-mentioned this invention for the comparison, and also the same electrode (operation pole for a comparison) was created like the case of the operation pole of above-mentioned this invention. Thus, after neglect aging of the produced cell was carried out for one week at the room temperature, the below-mentioned charge and discharge test was performed. Since alloying advanced enough and the lithium foil served as a Li-aluminum alloy altogether substantially according to this aging when the lithium-aluminum laminating electrode of a counter electrode touches nonaqueous electrolyte within a cell, cell voltage became the value which fell by about 0.4v compared with the case where a metal lithium is independently used as a counter electrode, and was stabilized.

[0021] Thus, hereafter, it corresponds to the active materials 1 and 4 of each used operation pole, and the produced cell is written as cells 1 and 4. The discharge property

of 3 cycle eye when performing these cells 1 and 4 by 1mA constant current, and performing a charge-and-discharge cycle on condition that termination electrical-potential-difference-0.4V of charge (the direction of a current which carries out the cell reaction by which occlusion of the lithium ion is carried out to an operation pole out of an electrolyte), and termination electrical-potential-difference 2.5V of discharge (the direction of a current which carries out the cell reaction by which a lithium ion is emitted into an electrolyte from an operation pole) was shown in drawing 2 , and the charge property was shown in drawing 3 . Moreover, the cycle property was shown in drawing 4 . In addition, the charge-and-discharge cycle was started from charge. The cell 1 by this invention has a remarkably large charge-and-discharge capacity compared with the comparison cell 4, and it turns out that the reversible field of charge and discharge is expanded remarkably so that clearly from drawing 2 -4. Moreover, the fall (cycle degradation) of the discharge capacity by the repeat of charge and discharge is remarkably small. Furthermore, it crosses to all charge-and-discharge fields, the difference of the operating potential of charge and discharge is remarkably small, and it turns out that polarization (internal resistance) of a cell is remarkably small, and high current charge and discharge are easy.

[0022] (Example 2) Instead of the active material 1 of an example 1, it is commercial barium titanate BaTiO_3 . What carried out the grinding particle size regulation to the particle size of 53 micrometers or less was used as an active material (active material 2 by this invention) of an operation pole. Except [all] the active material of this operation pole, the same cell 2 as well as the cell 1 of an example 1 was produced.

[0023] Thus, about the cell 2 and the above-mentioned comparison cell 4 which were obtained, the charge-and-discharge cycle trial was performed by 1mA constant current on condition that termination electrical-potential-difference-0.4V of charge, and termination electrical-potential-difference 2.5V of discharge. The discharge property of 3 cycle eye at this time was shown in drawing 2 , and the charge property was shown in drawing 3 .

[0024] Drawing shows that the cell 2 of this example has the charge-and-discharge property which was excellent like the cell 1 which depends on this invention of an example 1 like [it is ***** and]. Namely, multiple oxide $\text{Li}_x\text{BaTiO}_3$ which a lithium ion is therefore emitted to charge into an electrolyte from the Li-aluminum alloy of a counter electrode, this lithium ion moves in the inside of an electrolyte, electrode reaction is carried out to the active material 2 of an operation pole, and occlusion of the lithium ion is electrochemically carried out to an active material 2, and contains a lithium It generates. Next, it depends on a lithium ion being emitted into an electrolyte from this multiple oxide on the occasion of discharge, moving in the inside of an electrolyte, and occlusion being carried out into the Li-aluminum alloy of a counter electrode, and charge and discharge can be repeatedly carried out to stability. Here, an active material 2 is the multiple oxide $\text{Li}_x\text{BaTiO}_3$ which contains a lithium by 1st charge. It is multiple oxide $\text{Li}_x'\text{BaTiO}_3$ which contains a lithium in the cycle of subsequent discharge-charge in addition to the time of full discharge after generating. It forms.

[0025] (Example 3) What carried out the grinding particle size regulation of the commercial titanate-acid manganese MnTiO_3 to the particle size of 53 micrometers or less was used as an active material (active material 3 by this invention) of an operation pole. Except [all] the active material of this operation pole, the same cell 3 as well as the cell 1 of an example 1 was produced. Thus, about the cell 3 and the above-mentioned

comparison cell 4 which were obtained, the charge-and-discharge cycle trial was performed by 1mA constant current on condition that termination electrical-potential-difference-0.4V of charge, and termination electrical-potential-difference 2.5V of discharge. The discharge property of 1 cycle eye at this time was shown in drawing 2 , and the charge property was shown in drawing 3 .

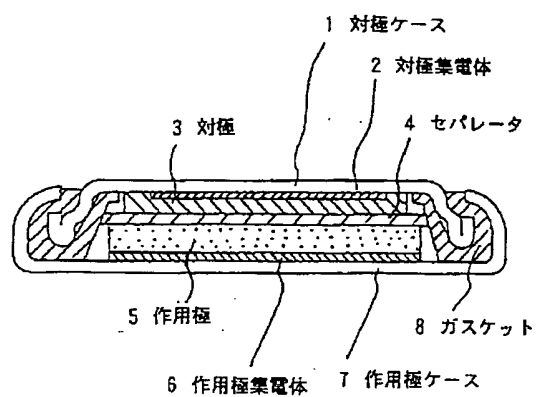
[0026] Drawing shows that the cell 3 of this example has the charge-and-discharge property which was excellent like the cells 1 and 2 which depend on this invention of examples 1 and 2 like [it is ***** and]. The cell 3 by this invention has a remarkably large charge-and-discharge capacity compared with the comparison cell 4, and it turns out that the reversible field of charge and discharge is expanded remarkably so that clearly from drawing 2 -3. Moreover, it crosses to all charge-and-discharge fields, the difference of the operating potential of charge and discharge is remarkably small, and it turns out that polarization (internal resistance) of a cell is remarkably small, and high current charge and discharge are easy.

[0027] Moreover, it turns out that the active materials 1, 2, and 3 of the cells 1, 2, and 3 which depend on this invention are excellent especially as a negative-electrode active material of a nonaqueous electrolyte rechargeable battery since the charge-and-discharge capacity of the **** potential field of -0.4-+0.6V (it corresponds to Abbreviation 0-1V to a metal lithium) is large to a Li-aluminum alloy electrode.

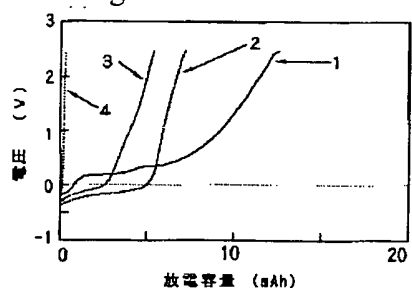
[0028] In addition, in an example, although only the case of a lithium-aluminium alloy was shown as a counter electrode This invention is not limited to an example. As mentioned above TiS₂, MoS₂, the metal chalcogen ghost of NbSe₃ grade, The metallic oxide of MnO₂, MoO₃, V₂O₅, LiXCoO₂ and LiXNiO₂, and Li_xMn₂O₄ grade, Conductive polymers, such as the poly aniline, polypyrrole, poly para-phenylene, and the poly acene, It cannot be overemphasized that the positive electrode which uses as an active material the matter which can occlusion emit the lithium cation and/or anion like **, such as intercalated graphite, can be used combining the negative electrode which considers as a counter electrode and depends on this invention.

[0029]

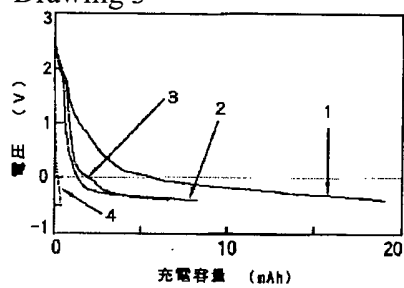
[Effect of the Invention] To the appearance explained in full detail above, this invention is an empirical formula RMO₃ as an active material of the negative electrode of a nonaqueous electrolyte rechargeable battery. The oxide of ***** perovskite type structure or multiple oxide Li_xRMO₃ which this is made to contain a lithium and is obtained The new active material which changes is used. from -- this multiple oxide Since [remarkable, the amount, i.e., the charge-and-discharge capacity, which can carry out occlusion emission of the lithium ion reversibly by charge and discharge in the **** potential field of 0-1V to a lithium criteria pole (metal lithium), / large and] polarization of charge and discharge is small, The rechargeable battery in which are high potential and a high energy consistency, and the charge-and-discharge property in a high current was excellent can be obtained. Moreover, degradation by overcharge overdischarge is hardly seen, but it has the ***** effectiveness -- it is very stable and the long cell of a cycle life can be obtained.



Drawing 2



Drawing 3



Drawing 4

